

20030221186

ADA235874

REPORT DOCUMENTATION PAGE			Form Approved OMB No. 0704-0188	
<small>Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.</small>				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE April 91	3. REPORT TYPE AND DATES COVERED Final Report 10/89 - 9/90		
4. TITLE AND SUBTITLE The Chemical Resistance of Protective Handwear Available Through The Navy's Supply System		5. FUNDING NUMBERS  62-1-70		
6. AUTHOR(S)  Andra Kirsteins		8. PERFORMING ORGANIZATION REPORT NUMBER  Technical Report No. NCTRF 184		
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)  Navy Clothing and Textile Research Facility P.O. Box 59 Natick, MA 01760-0001		10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)		11. SUPPLEMENTARY NOTES		
12a. DISTRIBUTION AVAILABILITY STATEMENT  Approved for public release; distribution unlimited		12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words)  The Navy Clothing and Textile Research Facility (NCTRF) evaluated seven types of chemical protective gloves, available through the Navy's supply system, for their chemical resistance against a selected list of 10 hazardous chemicals found aboard ship. The purpose of this study was to generate information that could be used in the development of a material for multi-purpose hazardous-chemical protective handwear. Such a glove would eliminate the need for a variety of gloves in the supply system that are procured for a specific use. It should be noted that these gloves were not tested for their intended uses, since this was not the scope of the study. The study revealed that none of the current gloves protects against all of the tested chemicals. Results from this study further justify the need for the development of a multi-purpose hazardous-chemical protective glove material.				
14. SUBJECT TERMS  Handwear; multipurpose protective handwear; chemical resistance; rubber; elastomers		15. NUMBER OF PAGES 28		
17. SECURITY CLASSIFICATION OF REPORT Unclassified		16. PRICE CODE		
18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT		

AD-A235 874



## Table of Contents

	<u>Page</u>
List of Tables. . . . .	iv
Introduction. . . . .	1
Theory. . . . .	1
Experimental. . . . .	3
Results and Discussion. . . . .	6
Conclusions and Recommendations. . . . .	24
Appendix A. References. . . . .	A-1



Accession For	
NTIS GRA&I	<input checked="" type="checkbox"/>
DTIC TAB	<input type="checkbox"/>
Unannounced	<input type="checkbox"/>
Justification	
By	
Distribution/	
Availability Codes	
Avail and/or	
Dist Special	
A-1	

# LIST OF TABLES

<u>Table</u>	<u>Page</u>
I Chemical Protective Gloves. . . . .	4
II List of Hazardous Chemicals . . . . .	5
III Chemicals Used in Absorption and Degradation Tests. . . . .	5
IV Absorption Data from Immersion of Four Butyl Gloves in Acetone. . . . .	7
V Absorption Data from Immersion of Four Butyl Gloves in Concentrated Ammonium Hydroxide. . . . .	8
VI Absorption Data from Immersion of Four Butyl Gloves in Amyl Acetate . . . . .	9
VII Absorption Data from Immersion of Four Butyl Gloves in Diethylether . . . . .	10
VIII Absorption Data from Immersion of Butyl Gloves in Hexane. . . . .	11
IX Absorption Data from Immersion of Butyl Gloves in Methanol. . . . .	12
X Absorption Data from Immersion of Butyl Gloves in Methyl Ethyl Ketone . . . . .	13
XI Absorption Data from Immersion of Butyl Gloves in Sulfuric Acid (70% aq). . . . .	14
XII Absorption Data from Immersion of Butyl Gloves in Toluene . . . . .	15
XIII Absorption Data from Immersion of Butyl Gloves in Trichloroethylene . . . . .	16
XIV Dimensional Change Following Immersion in Acetone . . . . .	17
XV Dimensional Change Following Immersion in Concentrated Ammonium Hydroxide . . . . .	17
XVI Dimensional Change Following Immersion in Amyl Acetate . . . . .	18
XVII Dimensional Change Following Immersion in Diethylether. . . . .	18
XVIII Dimensional Change Following Immersion in Hexane. . . . .	19

# LIST OF TABLES (Cont.)

<u>Table</u>		<u>Page</u>
XIX	Dimensional Change Following Immersion in Methanol. . . . .	19
XX	Dimensional Change Following Immersion in Methyl Ethyl Ketone. . . . .	20
XXI	Dimensional Change Following Immersion in Sulfuric Acid (70% aq) . . . . .	20
XXII	Dimensional Change Following Immersion in Toluene .	21
XXIII	Dimensional Change Following Immersion in Trichloroethylene . . . . .	21
XXIV	Gloves Meeting NCTRF Chemical Resistance "Pass" Criteria for Certain Chemicals <sup>2</sup> . . . . .	22

## THE CHEMICAL RESISTANCE OF PROTECTIVE HANDWEAR AVAILABLE THROUGH THE NAVY'S SUPPLY SYSTEM

### INTRODUCTION

The Navy Clothing and Textile Research Facility (NCTRF) has evaluated seven types of chemical protective gloves, available through the Navy's supply system, for their resistance to 10 hazardous chemicals found aboard ship. Each glove is intended for different uses, but many are made of identical materials. The objective was to determine which, if any, of these gloves would show promise as a candidate for a multi-purpose hazardous-chemical protective glove. Such a glove would eliminate the need for the different types of gloves currently in the supply system, and thus help alleviate shipboard storage problems. NCTRF conducted chemical degradation and solubility tests on samples of each glove type, using a variety of hazardous chemicals found aboard ship. Results from the laboratory evaluation showed the butyl rubber gloves to be the most resistant against the chemicals tested, but this resistance is limited only to the ketones and to the alcohol, acid and base tested. None of the tested gloves provides resistance to any of the other chemicals. Because of the lack of general chemical resistance of the gloves currently in the supply system, none of them was found to be a suitable candidate for a multi-purpose hazardous-chemical protective glove. Therefore, NCTRF recommends that a new glove be developed. The information gained from this study will aid in the development of a new glove. This report discusses laboratory test findings.

### THEORY

All elastomeric/polymeric materials have some degree of permeability to all chemicals. A chemical can pass through chemical protective clothing in three ways: by penetrating, permeating or degrading the material.

Penetration is the bulk flow of chemical through the material, which can happen through pin holes in the material, poorly sealed seams, etc. Chemical penetration can be avoided by proper design of chemical protective clothing and the material itself.

On the other hand, in chemical permeation, the chemical moves through the material on a molecular basis by a process known as diffusion. There are three steps in permeation. (1) The chemical must have enough energy to leave the medium (this is known as vapor pressure) and absorb into the material. (2) The chemical then diffuses through the material and (3) vaporizes from the backside of the material.

The rate controlling step in permeation is the diffusion process. The driving force for diffusion is the difference in partial pressure, or concentration, of the chemical, which is related through the vapor pressure of the chemical across the material. The diffusion process usually can be mathematically represented by Fick's laws of diffusion, which are given as follows, assuming one-dimensional diffusion:

$$J = -D \frac{dc}{dx} \text{ (steady state)}$$
$$\frac{dc}{dt} = D \frac{d^2c}{dx^2} \text{ (un-steady state) [1],}$$

where  $J$  is the flux (grams/cm<sup>2</sup>/sec),  $c$  is concentration (grams of chemical/gram of permeated material),  $x$  is distance into the material (cm), or thickness of material, and  $D$  (grams/cm<sup>2</sup>/sec) is the diffusion coefficient.  $D$  can be determined experimentally for Fickian diffusion. The diffusion coefficient varies with temperature and is a function of the tightness or degree of cross-linking of the polymer and the number of adsorption sights for the molecules on the polymer chains. Once all adsorption sights are filled and the polymer can no longer hold any additional molecules, it is termed "saturated". This value is known as  $S$ , the maximum solubility or saturation point. The saturation point can also be determined experimentally. Weight gain measurements taken periodically, for an immersed sample, give an indication of solubility and, in certain cases, can be used to predict permeation rates.

Permeability is defined as the product of the diffusion coefficient and solubility. A material with a very low diffusion coefficient may not necessarily provide the desired level of protection if coupled with a very high solubility. The permeation rate or breakthrough time is typically evaluated using ASTM F739<sup>1</sup>. The material is placed in a cell with the outer side of the garment exposed to the chemical. Any chemical that permeates and vaporizes from the underside of the garment is swept away by a collecting medium that is analyzed by a detector.

Permeation testing is expensive and time consuming. In order to minimize the number of permeation tests that must be conducted, a much simpler evaluation procedure, that should be used only for screening, is a degradation test. If a material degrades, ie. swells, when exposed to a chemical, it certainly will not provide protection against it. However, the converse of this is not true. Degradation is defined as a loss or change in one or more physical properties of the material. Examples of visual signs of degradation are swelling, cracking, tackiness, softening, hardening, color change, flaking and blistering [2].

---

<sup>1</sup>American Society for Testing Materials. Test Method F739-85, Resistance of Protective Clothing Materials to Permeation by Hazardous Liquid Chemicals, Vol 15:07.

Swelling measurements are commonly used as a measure of the degree of chemical resistance. A polymer swells when it absorbs very large quantities of chemical. The reason why a polymer or elastomer can absorb very large quantities of liquid is that the chemical dissolves, or mixes spontaneously with the polymer. Dilution forces cause absorption. However, because the three-dimensional network polymer cannot disperse completely, the chains assume an elongated configuration. The farther the chains are pulled apart, the more chemical the polymer can absorb, which results in more swelling. There is a maximum or equilibrium amount of swelling that the material can undergo. Equilibrium is the point at which dilution forces equal the retractive force of the polymeric network. This value is temperature dependent [3,4].

#### EXPERIMENTAL

Table I lists the evaluated gloves. Table II lists the 30 chemicals that the hazardous chemical protective glove should protect against. However, due to the difficulty of working with some of the chemicals, a selected group of only 10 chemicals was chosen for testing. These chemicals are listed in Table III.

Because conducting a chemical permeation test on every type of glove with each chemical was too time-consuming, it was of interest to reduce the number of these tests. Since a simple degradation test would accomplish this result, chemical degradation and solubility tests were conducted to screen which government-issued glove/chemical combinations should be subjected to chemical permeation testing.

For each glove type, ten 1-square-inch samples were cut randomly from 10 glove pairs. The samples were weighed and planar dimensions and thickness were measured. The thickness was measured with a CSI Thickness Gauge, with a 3/4" diameter pressure foot and a load of 18 ounces. Planar dimensions were simply measured with a ruler. Three samples from each glove type were immersed in each of the test chemicals at room temperature, which ranged from 18 to 23 degrees Celsius. Weight measurements were taken periodically. The samples were removed from the chemical and blotted dry very quickly in order to remove any free chemical from the surface. The samples were then weighed immediately in order to minimize inaccuracies due to desorption from the rubber sample. Visual changes in the material were noted as well. The experiment was terminated if the material cracked, fell apart, or hardened and curled up so much that it could not be measured. At the end of the test, dimensional changes were measured immediately following removal from the chemical.

Weight gain measurements were not taken for those glove samples possessing a cloth backing. Because these gloves had been manufactured using a dipping process, the cloth could not be



Table I. Chemical Protective Gloves

<u>Specifica- tion #</u>	<u>Nomenclature</u>	<u>Material</u>	<u>Average Material Thickness (mils)</u>
Mil ZZ-G-381	Gloves, R u b b e r , Industrial, Type III	butyl rubber	48.0
Mil G-12223	Gloves, Tox- icological A g e n t s Protective	butyl rubber	33.9
Mil G-21854	Gloves, Pro- tective, Fuel and Oxidizer Resistant	butyl rubber	35.3
Mil G-87033*	M i t t e n Set, Extreme Cold Weather	neoprene rubber**	32.3
Mil G-43196	Gloves, Rocket Fuel Handlers	polyvinyl chloride**	47.8
Mil G-43976	Gloves, Chemical Protective (Type I)	butyl rubber	24.7
Mil G-82253	Gloves, Cloth, Vinyl Dipped, G e n e r a l Purpose (avi- ation fuel, hydrogen peroxide, oils)	polyvinyl chloride**	54.8

\* Mitten is not considered a chemical protective glove, although it has some POL protection.

\*\* Material has a cloth backing.

Table II. List of Hazardous Chemicals

Acetone  
Ammonium Hydroxide  
Aviation Fuels (JP-4 & JP-5)  
Carbon Disulfide  
Cellosolve (Ethyl moroethyl ether)  
Diethylamine  
Diethylether  
Dimethylsulfoxide (DMSO)  
Epichlorohydrin  
Ethyl Acetate  
Freon TF  
Hexane  
Hydraulic Fluids  
Hydrazine  
Hydrochloric Acid  
Methanol  
Methyl Ethyl Ketone (MEK)  
Methyl Methacrylate  
Naphthalene  
Nitric Acid  
Nitrobenzene  
OTTO Fuel  
Pentachlorophenol  
Sodium Hydroxide  
Styrene  
Sulfuric Acid (fuming)  
Tetrahydrofuran  
Toluene  
Trichloroethylene

Table III. Chemicals Used in Absorption and Degradation Tests

Acetone  
Ammonium Hydroxide (concentrated)  
Amyl Acetate (ester substitute)  
Diethylether  
Hexane  
Methanol  
Methyl Ethyl Ketone (MEK)  
Sulfuric Acid (70% solution)  
Toluene  
Trichloroethylene

removed entirely and, therefore, only dimensional changes could be recorded. The chemical absorbed by the cloth would have provided misleading results.

The absorption and degradation test results were divided into three groups: (1) those showing greater or less than a 10% weight gain over the course of the experiment; (2) those showing swelling or no swelling; and (3) those showing deterioration (excluding swelling).

## RESULTS AND DISCUSSION

Tables IV to XIII give the weight change results for each butyl glove/chemical combination tested at various time intervals. Tables XIV to XXIII show the dimensional changes for all glove/chemical combinations. Results represent the average of three tested samples.

Any material showing appreciable swelling, in either thickness or planar dimensions, was automatically designated as being degraded by that chemical. A rule of thumb used by many is that, if a material absorbs greater than 10% of its initial weight over a time interval, it will not provide the user with protection against the chemical for that period of time [5,6]. The gloves are desired to provide the user with chemical protection for the length of one 8-hour shift. Most of the gloves were tested for a maximum of only 6 hours in order to complete the experiments within a work day. NCTRF determined this length of time to be sufficient, since those gloves that did fail, failed much sooner than 6 hours. Those that passed did not show much change in the amount of chemical absorbed after 6 hours, meaning that the samples were at, or close to, saturation. (Chemical absorption into a material ceases when it becomes saturated. The saturation point is reported as the maximum (equilibrium) amount of chemical absorbed per weight of polymer. The samples that were passed had saturation values well below the 10% failure criterion.) It should be noted that all glove samples that did swell absorbed greater than 10% of initial weight of chemical. Table XXIV summarizes which glove/chemical combinations met this criterion.

Because of the volatility of some of the chemicals used, the samples would lose weight during the weighing process. Consequently, the samples had to be blotted dry very quickly and the weight recorded immediately after the sample was placed on the balance. This resulted in some variability in the data. Other possible causes of data variability could be improper drying of the sample and/or temperature variations. The rate of permeation roughly doubles for every 10 degrees celsius temperature change.

Some of the glove materials exhibited a weight loss when subjected to certain chemicals, which the data indicates by a negative weight gain. This could be due to the extraction of plasticizers or other additives. Loss of additives could be

Table IV. Absorption Data from Immersion of Four Butyl Gloves in Acetone. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43076
30	6.9	0.3	-0.2	0.2
60	10.1	0.4	-0.1	0.4
90	15.3	---	---	0.6
120	---	---	---	---
150	---	0.6	0.2	---
180	---	---	---	---
210	---	---	0.35	---
240	17.2	---	---	0.8
270	---	0.9	0.5	---
330	---	1.0	---	---
360	17.8	---	---	1.1

Table V. Absorption Data from Immersion of Four Butyl Gloves in Concentrated Ammonium Hydroxide. (Wt. chemical absorbed/ wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	---	---	---	---
60	1.2	0.0	0.0	0.1
90	---	---	---	---
120	---	---	---	---
150	---	---	---	---
180	---	---	---	---
210	2.2	0.0	0.1	0.3
240	---	---	---	---
270	---	---	---	---
330	---	---	---	---
360	2.8	0.1	0.1	0.4

Table VI. Absorption Data from Immersion of Four Butyl Gloves in Amyl Acetate. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	75.4	12.0	11.9	16.0
60	12.9	15.2	15.7	28.1
90	---	20.9	---	40.3
120	---	---	---	---
150	---	26.7	26.7	---
180	177.2	30.3	34.0	---
210	---	---	---	---
240	191.4	---	38.6	40.6
270	---	---	---	---
330	---	---	---	---
360	199.6	---	---	40.2

Table VII. Absorption Data from Immersion of Four Butyl Gloves in Diethylether. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-331	G-12223	G-21854	G-43976
30	122.9	52.6	50.2	52.4
60	---	---	---	---
90	---	57.1	55.4	50.3
120	---	---	---	---
150	---	---	---	---
180	---	---	---	---
210	137.0	56.4	55.3	50.1
240	---	---	---	---
270	145.3	56.6	55.5	51.0
330	---	---	---	---
360	---	57.1	55.8	51.1

Table VIII. Absorption Data from Immersion of Butyl Gloves in Hexane. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	---	106.2	110.8	---
60	---	---	---	115.9
90	128.6	126.0	142.9	121.9
120	---	---	---	---
150	---	---	---	---
180	162.4*	126.2	144.1	---
210	---	---	---	---
240	---	125.7	145.3	122.7
270	---	---	---	---
330	---	---	---	---
360	---	---	---	119.1

\* Softened and fell apart during handling



Table IX. Absorption Data from Immersion of Butyl Gloves in Methanol. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	0.5	0.0	-0.1	0.0
60	0.8	0.0	-0.2	0.0
90	---	0.0	---	---
120	1.1	---	-0.2	---
150	---	---	-0.3	0.0
180	---	0.0	---	---
210	---	---	---	-0.3
240	1.6	0.0	-0.3	---
270	---	---	---	---
330	---	---	---	---
360	2.1	---	-0.4	---

Table X. Absorption Data from Immersion of Butyl Gloves in Methyl Ethyl Ketone. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	21.8	1.1	0.4	0.9
60	57.8	1.6	0.5	---
90	---	2.0	---	---
120	---	2.3	---	---
150	---	---	1.5	2.6
180	---	2.9	---	---
210	---	3.2	---	---
240	---	---	---	---
270	---	3.8	---	3.2
330	---	4.1	2.3	4.0
360	---	4.8	---	---

Table XI. Absorption Data from Immersion of Butyl Gloves in Sulfuric Acid (70% aq). (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	---	---	---	---
60	1.6	---	0.0	0.0
90	---	---	---	---
120	---	---	---	---
150	---	---	---	---
180	2.6	0.0	0.0	0.0
210	---	---	---	---
240	---	---	---	---
270	---	---	---	---
330	3.8	0.0	0.0	0.0
360	---	---	---	---

Table XII. Absorption Data from Immersion of Butyl Gloves in Toluene. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	---	111.1	96.3	---
60	---	138.3	---	141.8
90	249.3*	---	---	147.9
120	---	154.9	169.4	---
150	---	156.8	179.0	---
180	259.7	157.4	---	155.7
210	---	---	---	---
240	---	---	183.6	150.4
270	---	---	---	---
330	---	---	---	---
360	---	---	---	150.8

\* Softened and cracked during handling

Table XIII. Absorption Data from Immersion of Butyl Gloves in Trichloroethylene. (Wt. chemical absorbed/wt. material) x 100%.

Time(min)	Mil-			
	ZZ-G-381	G-12223	G-21854	G-43976
30	---	309.0	407.2	---
60	332.1*	397.9	---	355.8
90	---	414.8	499.4	---
120	---	420.2	---	---
150	---	423.9	527.9*	394.1*
180	---	424.2	---	---
210	---	422.9	536.7	---
240	---	---	---	---
270	---	433.6	---	---
330	---	---	---	---
360	---	422.2	---	386.2

\* Softened and cracked during handling

Table XIV. Dimensional Change Following Immersion in Acetone

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	360	5.6	12.5
G-12223	Butyl	330	-0.2	1.6
G-21854	Butyl	360	6.6	0.9
G-43976	Butyl	360	-2.9	0.8
G-82253	PVC	---	---	---
G-43196	PVC	---	---	---
G-87033	Neoprene	360	39.0	26.8

Table XV. Dimensional Change Following Immersion in Concentrated Ammonium Hydroxide

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	360	-1.2	0.1
G-12223	Butyl	360	-3.7	-0.3
G-21854	Butyl	360	-8.1	-0.2
G-43976	Butyl	360	-4.7	-0.4
G-82253	PVC	330	0.9	0.8
G-43196	PVC	330	2.1	-1.9
G-87033	Neoprene	330	-4.1	0.1

Table XVI. Dimensional Change Following Immersion in Amyl Acetate

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	360	45.1	112.1
G-12223	Butyl	180	12.6	18.4
G-21854	Butyl	240	28.5	28.5
G-43976	Butyl	360	13.4	32.9
G-82253*	PVC	---	---	---
G-43196*	PVC	---	---	---
G-87033	Neoprene	150	7.6	102.0

\* Hardened and shrank

Table XVII. Dimensional Change Following Immersion in Diethylether

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	360	44.3	105.2
G-12223	Butyl	360	24.0	60.0
G-21854	Butyl	360	14.8	45.5
G-43976	Butyl	360	17.4	45.5
G-82253*	PVC	330	-9.1	-26.7
G-43196*	PVC	330	-2.1	-22.1
G-87033	Neoprene	330	13.4	49.3

\* Hardened and shrank

Table XVIII. Dimensional Change Following Immersion in Hexane

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381*	Butyl	180	49.6	124.9
G-12223	Butyl	240	47.2	97.4
G-21854	Butyl	240	45.5	112.1
G-43976	Butyl	360	47.0	100.3
G-82253**	PVC	---	---	---
G-43196**	PVC	---	---	---
G-87033	Neoprene	150	3.1	14.3

\* Softened and fell apart during handling

\*\* Hardened and shrank

Table XIX. Dimensional Change Following Immersion in Methanol

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	330	3.3	0.4
G-12223	Butyl	240	-0.8	0.4
G-21854	Butyl	240	1.0	-0.5
G-43976	Butyl	270	1.1	-1.8
G-82253*	PVC	330	-2.9	-4.3
G-43196*	PVC	330	-0.9	-5.0
G-87033	Neoprene	180	23.6	1.6

\* Hardened slightly



Table XX. Dimensional Change Following Immersion in Methyl Ethyl Ketone

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	---	---	---
G-12223	Butyl	360	2.2	4.0
G-21854	Butyl	405	5.2	2.4
G-43976	Butyl	405	0.7	1.6
G-82253	PVC	---	---	---
G-43196	PVC	---	---	---
G-87033	Neoprene	240	37.3	66.9

Table XXI. Dimensional Change Following Immersion in Sulfuric Acid (70% aq)

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w)(%)</u>
Mil-				
ZZ-G-381	Butyl	300	0.9	-0.8
G-12223	Butyl	300	3.3	-1.3
G-21854	Butyl	300	0.1	0.8
G-43976	Butyl	300	1.3	-0.9
G-82253	PVC	270	-13.7	-0.5
G-43196	PVC	300	-12.6	1.6
G-87033	Neoprene	270	-8.8	0.0

Table XXII. Dimensional Change Following Immersion in Toluene

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w) (%)</u>
Mil-				
ZZ-G-381*	Butyl	180	65.3	171.4
G-12223	Butyl	180	40.5	106.1
G-21854	Butyl	210	47.9	114.0
G-43976	Butyl	360	61.3	95.3
G-82253**	PVC	180	-7.6	-4.3
G-43196**	PVC	180	0.0	-1.7
G-87033	Neoprene	180	22.4	155.8

\* Softened and fell apart during handling

\*\* Hardened slightly

Table XXIII. Dimensional Change Following Immersion in Trichloroethylene

<u>Glove Spec.</u>	<u>Type</u>	<u>Immersion Time(min)</u>	<u>Thickness Change(%)</u>	<u>Planar Dimension Change (l x w) (%)</u>
Mil-				
ZZ-G-381*	Butyl	60	---	---
G-12223	Butyl	360	57.2	154.3
G-21854	Butyl	210	67.0	178.9
G-43976	Butyl	360	68.5	153.1
G-82253**	PVC	180	-11.3	-11.2
G-43196**	PVC	210	-0.8	-7.2
G-87033*	Neoprene	150	49.0	156.4

\* Softened and fell apart during handling

\*\* Hardened and shrank

Table XXIV. Gloves Meeting NCTRF Chemical Resistance "Pass"  
Criteria for Certain Chemicals<sup>2</sup>

<u>Acetone</u>	<u>Ammonium</u> <u>Hydroxide</u>	<u>Methanol</u>	<u>Methyl</u> <u>Ethyl</u> <u>Ketone</u>	<u>Sulfuric</u> <u>Acid</u>
Mil-G-	Mil-	Mil-	Mil-G-	Mil-G-
12223	G-12223	G-12223	12223	12223
21854	G-21854	G-21854	21854	21854
43976	G-43976	G-43976	43976	43976
	ZZ-G-381	ZZ-G-381		82253
	G-82253			87033
	G-87033			43196
	G-43196			

<sup>2</sup>Any glove that showed less than a 10% weight gain and did not swell or deteriorate.

critical to the material's protective or functional properties. Without further experimentation, it cannot be determined if these small weight losses have had any effect. It is important to note that when a polymer absorbs a chemical, it may be simultaneously extracting additives. This can be determined by performing an absorption/desorption/re-adsorption experiment, which was beyond the scope of this work.

Except for specification number Mil ZZ-G-381, all butyl gloves appear to show little or no effect when exposed to the ketones and to the alcohol, acid and base tested. However, as expected, chemical resistance dropped from acetone to methyl ethyl ketone, since the more non-polar the chemical, the more it affects the solubility of the butyl rubber [3]. With a neoprene-type material, the effect should be reversed due to the increased polarity of the polymeric chains. The neoprene glove material showed to be resistant only to the acid and base, as did the polyvinyl chloride (PVC) based gloves. The PVC gloves did not swell, but shrank and hardened to some degree. A polymer will shrink when exposed to a chemical that it is not soluble in. Because the polymer doesn't "like" the chemical, it will try to keep it out by curling the polymeric chains, resulting in a more tightened structure [3]. This is what causes it to shrink and harden.

It should be noted the Mil ZZ-G-381 butyl glove is significantly thicker than the other butyl gloves and it was the only glove material that contained no carbon black as a filler. As discussed earlier, the permeation rate is a function of thickness. If two identical materials are taken, and the samples are of different thicknesses, it will take longer for any chemical to permeate the thicker sample material. The converse is seen with the Mil ZZ-G-381 glove material, which is clearly inferior to all other butyl glove materials tested. It is not known what fillers are contained in the Mil ZZ-G-381 butyl glove material, which is tan. Good quality inert fillers, such as carbon black, should improve the physical properties of the material, as well as the permeation rate [7]. The filler increases the tortuosity the permeating chemical must travel through the polymer, thus reducing the diffusion coefficient. Poor quality fillers, e.g., clays, may adsorb the chemical, and, hence, increase the permeation rate. When the Mil ZZ-G-381 glove was immersed in sulfuric acid, it turned a rust color. It is not known if this resulted from an interaction that occurred with the rubber, a filler, or an additive.

Because none of the results was normalized to thickness, it is difficult to make a comparison among the tested gloves. The thicker the material, the longer it will provide the user with chemical protection. Consequently, permeation testing will be conducted on the glove/chemical combinations listed in Table XXIV to establish the maximum length of time they can provide the user protection.

## CONCLUSIONS AND RECOMMENDATIONS

1. Butyl gloves conforming to specification numbers Mil G-12223, Mil G-21854 and Mil G-43976 showed the best protection of all tested gloves, but only when subjected to the ketones, and to the alcohol, acid and base tested. Generally speaking, all gloves performed poorly when subjected to the balance of the chemicals.
2. Based on dimensional change data, the Mil G-87033 neoprene glove material appeared to be chemically resistant to concentrated ammonium hydroxide and sulfuric acid (70% aq).
3. Specification number Mil ZZ-G-381 butyl glove material is inferior to the other three butyl gloves tested. This could be due to the starting materials, manufacturing/cure process, additives, fillers and, possibly, storage time of the glove.
4. The PVC gloves appeared to be resistant only to the acid and base tested.
5. Permeation may occur without signs of degradation. For this reason permeation tests must be conducted to determine how long the user can be provided with chemical protection. A contract has been awarded to conduct permeation testing.
6. Since none of the tested gloves was resistant to the ester, chlorinated hydrocarbon, alkane, aromatic and ether tested, a glove material needs to be developed which can protect against all of these chemical classes.

**NOTE:** NCTRF has subsequently awarded a contract for the development of flame-retardant multi-purpose chemical protective handwear that can protect Navy personnel against various types of hazardous acids, bases, organic chemicals, fuels, oils and lubricants, which may be encountered in the shipboard environment.

#### APPENDIX A. REFERENCES

1. Crank, J. "The Mathematics of Diffusion," 2nd edition. Clarendon Press, Oxford, UK, 1975.
2. Stull, Jeffrey O. "Methods for Measuring the Chemical Resistance of Protective Clothing Material." Texas Research Institute, Inc. Report.
3. Flory, Paul J. "Principles of Polymer Chemistry". Cornell Univ. Press, Ithaca, N.Y., 1953, pp. 576-584.
4. Ridge, Michael C. and Jimmy L. Perkins, PhD. "Permeation of Solvent Mixture Through Protective Clothing Elastomers." Chemical Protective Clothing Performance in Emergency Response, ASTM STP 1037, Oct. 1989.
5. Bentz, Alan A. and Clare B. Billing. "Determination of Solubility Parameters of New Suit Materials." Performance of Protective Clothing, Second Symposium, ASTM STP 989, S.Z. Mansdorf, R. Sager and A.P. Nielsen, Eds., American Society for Testing and Materials, Philadelphia, 1988, pp. 208-218.
6. Pohlman, Teresa R. "Development of a Chemical Warfare Protective Dive Suit (CWPDWS) for United States Navy Diving in Contaminated Water." Chemical Protective Clothing Performance in Emergency Response, ASTM STP 1037, Oct. 1989.
7. Eirich, Frederick, R. "Science and Technology of Rubber." Academic Press, Inc., N.Y., 1978.